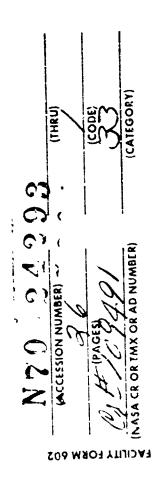


# PHYSICAL AND EXPLOSION CHARACTERISTICS OF HYDRAZINE NITRATE







UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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# PHYSICAL AND EXPLOSION CHARACTERISTICS OF HYDRAZINE NITRATE

By Harry K. James, Yael Miron, and Henry E. Perlee

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## PHYSICAL AND EXPLOSION CHARACTERISTICS OF HYDRAZINE NITRATE

by

Harry K. James, <sup>1</sup> Yael Miron, <sup>2</sup> and Henry E. Perlee<sup>3</sup>

#### ABSTRACT

Experimental studies of the physical and explosion characteristics of pure hydrazine nitrate and multicomponen' systems containing hydrazine nitrate, supplemented with an extensive literature survey, are presented. Such properties as melting point, heat of fusion, density, viscosity, surface tension, thermal stability, dec mosition process, detonation velocity, impact sensitivity, and TNT equivalence are included.

#### INTRODUCTION

Hydrazine mitrate (HN) has been of considerable interest in explosives research since Curtius and Jay (6)<sup>4</sup> first prepared it in 1889. This interest has been primarily due to the fact that, having no carbon atoms, HN is a smokeless explosive. More recently, HN has become of interest in space propulsion studies. In cooperation with the National Aeronautics and Space Administration (NASA) Manned Spacecraft Center, the Bureau of Mines has compiled the available information on the physical and explosion characteristics of HN and multicomponent systems containing HN.

HN exists in two crystalline forms,  $\alpha$  and  $\beta$ . The  $\beta$  form is unstable, and except for the melting point, little is known about it. The data presented in this paper, therefore, concern only the  $\alpha$  form. This report describes only new apparatus and techniques. Where appropriate the work of other investigators is discussed and compared with the results obtained in Bureau research. The appendix of this paper presents, in tables and illustrations, a summary of physical properties of HN which were determined by other investigators.

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<sup>&</sup>lt;sup>4</sup>Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

## PREPARATION OF PURE HYDRAZINE NITRATE (HN)

The HN used in the Bureau experiments was prepared in the following manner. Commercial anhydrous hydrazine (97.5-percent purity) was dissolved in methanol (reagent grade, 99.9-percent purity) and cooled to about -20° C. Nitric acid (A.C.S. grade, 70-percent purity), also at -20° C, was then added in drops to the hydrazine-methanol solution while the temperature was carefully maintained below 9° C. The addition of acid was continued until a pH of 5.5 was reached. The white HN precipitated during the addition process was filtered off and melted in boiling methanol and recrystallized. This recrystallization step was repeated twice. The last trace of methanol was removed in vacuum, and the final salt was dried and stored in a vacuum desiccator over phosphorus pentoxide. Chemical analysis of the prepared crystals by the nitron nitrate precipitation technique (12) indicated that the purity of the HN was greater than 99.0 percent.

#### PHYSICAL PROPERTIES OF HN

## Crystalline Forms and Their Melting Points

HN exists in two crystalline forms,  $\alpha$  and  $\beta$ ; the stable  $\alpha$  form (crystal density, 1.661 g/cm<sup>3</sup>) melts at approximately 70° C (table A-1) with no apparent decomposition or sublimation. The unstable  $\beta$  form melts at 62° C.

## Heat of Conversion of the $\beta$ Form to the $\alpha$ Form

Robinson and McCrone (24) found that a melt of HN supercools readily and usually crystallizes as the unstable  $\beta$  form. Sommer (29) noted that HN exhibits monotropism; that is, the  $\beta$  form always converts to the  $\alpha$  form with the evolution of heat. Using differential scanning calorimetry techniques, the Bureau obtained a value of 2.0 kcal/mole for the heat of conversion of the  $\beta$  to the  $\alpha$  form. No additional thermal phase changes in the crystalline structure of the  $\alpha$  form have been found from -70° C to its melting point.

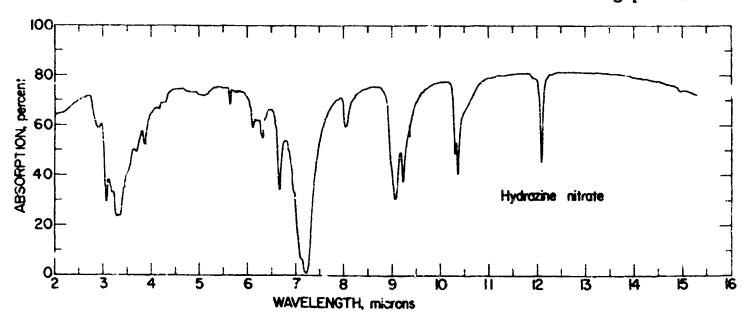


FIGURE 1. - Infrored Absorption Spectra for HN.

## Infrared and X-ray Spectra

or identification purposes the infrared absorption and X-ray diffraction spect: were obtained by the Bureau. These are shown in figure 1 and table 1, respectively.

I/I <sub>o</sub>	D,	I/I <sub>o</sub>	D,
20.6	4.42	8.6	2.10
80.2	3.98	22.2	2.05
27.2	3.59	27 . 7	1.91
100.0	3.25	13.8	1.87
17.8	2.89	12.7	1.68
59.5	2.69	9.9	1.52
33.2	2.40	17.6	1.42
9.2	2.34	1.39	1.39
23.9	2.24	1.37	1.37

TABLE 1. - X-ray diffraction spectra for HN

I/I = ratio of scattered-to-incident beam intensities.

D = wavelength of the scattered line.

## Weight-Loss Rate

Experiments were performed by the Bureau to measure the rate of loss of molten HN due to the combined effects of dissociation and decomposition by differential gravimetric techniques using 20-mg samples having surface areas of 0.20 cm2. At 250° C, the weight loss varied linearly with time and amounted to about 3 weight-percent per minute; at 200° C the rate was 4×10-1 weight-percent per minute, and at 150° C it was 6×10-2 weight-percent per minute. Because below 250° C more than 99 percent of the initial quantity of HN was recovered, the weight loss of HN is attributable entirely to a dissociation process. Medard (19), in similar work, determined the weight loss of anhydrous HN during intermittent heating to 110° C for 315 hours and found that it was linearly dependent with time, or about  $8 \times 10^{-5}$  weight-percent per minute. Kissinger (15) found that HN decomposition at 140° C was "barely noticeable by standard vacuum stability techniques." He also reported that HN could be stored under 95 percent ethyl alcohol at a maximum temperature of 30° C for as long as 4 months without any "apparent ill effects." Sabanejeff (26) found weight-loss rates of  $3\times10^{-3}$  and  $9\times10^{-2}$  weight-percent per minute at 145° and 215° C, respectively. The reason for the large discrepancy among the values obtained by the various researchers is unknown.

#### PHYSICAL PROPERTIES OF MULTICOMPONENT SYSTEMS CONTAINING HN

## Density of HN Solutions With Hydrazine and Water

The density of HN-hydrazine and HN-water solutions at various temperatures and HN concentrations was determined using a  $2\text{-cm}^3$  pycnometer. A constant-temperature oil bath was used to maintain the desired temperature within  $\pm 0.4^\circ$  C. Figures 2 and 3 show these results obtained by the Bureau.

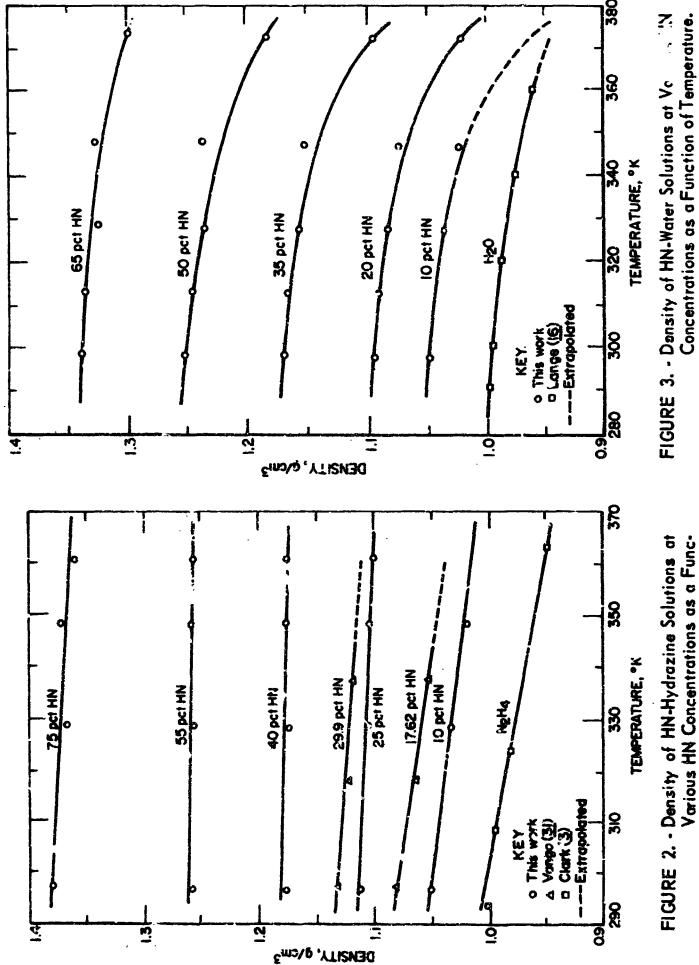


FIGURE 2. - Density of HN-Hydrazine Solutions at Various HN Concentrations as a Func-tion of Temperature.

Regression analysis of these data shows that the longities of these solutions, ranging in concentration from 10 to 75 weight-1 reent and in temperature from 25° to 100° C, can be adequately described by the relation,

$$\rho = \rho_0 + \epsilon \underline{N} + b \underline{N}^{\frac{1}{2}},$$

in which  $\rho$  and  $\rho_o$  are the densities of the solution and solvent, respectively, at the same temperature, N is the normality of the solution, and a and b are regression coefficients. For the HN-hydrazine solutions, a and b equal 0.027 and 0.032, respectively, and 0.036 and 0.018, respectively, for HN-water solutions.

Vango and Krasinsky (31) measured the density of two FN-hydrazine solutions, containing about 0.3 weight-percent uniline, as a function of temperature. Of the two solutions tested, one contained 17.62 weight-percent HN and the other contained 29.97 weight-percent HN. Figure 2 includes a plot of Vango and Krasinsky's results; for comparison, the temperature dependence of the density of pure hydrazine, taken from the work of Clark (5), and of water, taken from Lange (16), are shown in figures 2 and prescentively.

## Viscosity of HN Solutions With Hydrazine and With Water

The kinematic viscosity of molten HN and various HN-hydraxine and HN-water solutions as a function of temperature and HN concentration was measured with a Cannon-F nske viscometer in a constant temperature bath to maintain the desired temperature within ±0.4° C. The sults are shown in figures 4 and 5. Viscosity measurements of hydrazine are maluded in figure 4 for comparison. Regression analysis of the viscosity data for HN-bydrazine solutions gave the relation,

$$\log_{10} \frac{V}{V_0} = K \frac{N}{T},$$

in which V and  $V_0$  are the kinematic viscosities in centistokes of the solution and solvent, respectively, at absolute temperature, T, degrees Kelvin; N is the solution normality; and K is a regression coefficient equal to 24.59. In the case of PN-mater solutions, regression analysis of the data yielded the expression,

$$\log_{10} \frac{V}{V_0} = K \cdot \frac{N^2}{T} ,$$

in which K is 1.25. For comparison, figure 4 shows also the results obtained by Vango and Krazinsky for two HN-hydrazine solutions using a Cannon-Zhukov viscometer. The temperature dependence of the viscosity of pure hydrazine, taken from Lange (16) is also given in figure 4. There is good agreement between the Bareau results and the results obtained by Vango and Krasinsky (31).

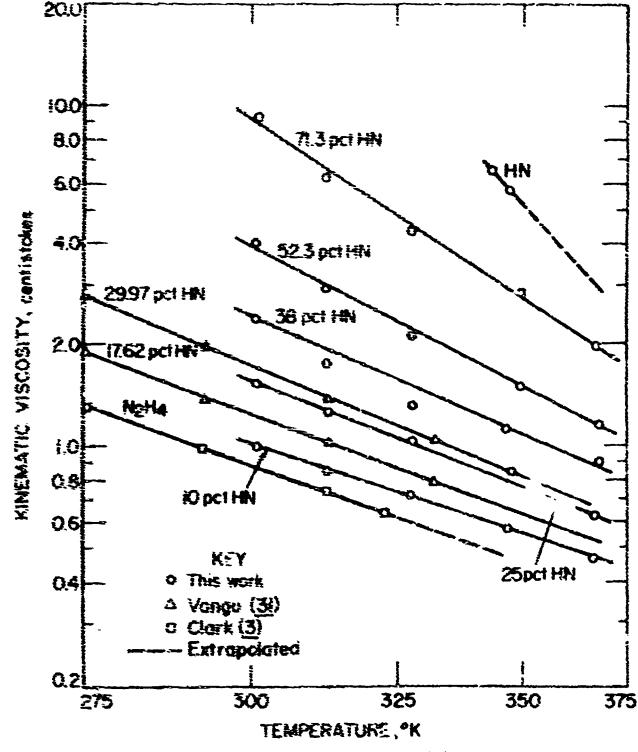


FIGURE 4. - Kinematic Viscosity of HN-Hydrazine Solutions at Various HN Concentrations as a Function of Temperature.

## Surface Tension of HR Solutions With Bydrazine and With Water

The Bureau also determined the surface tension of various HN-hydrazine and HN-water solutions at different temperatures. The bubble pressure method described by Partington (21) was used because surface contamination effects are minimized by this method. The surface tensions of molten HN and various HN-hydrazine and HN-water solutions at elevated temperatures were measured; the results are shown in figures 6 and 7. Regression analysis of these data

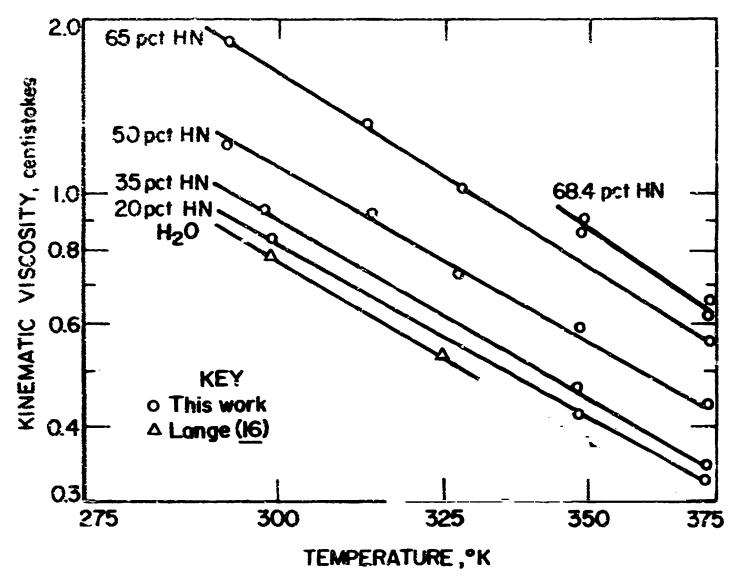


FIGURE 5. - Kinematic Viscosity of HN-Water Solutions at Various HN Concentrations as a Function of Temperature.

shows that the surface tension can be adequately described by the expression,

$$\gamma = \gamma_c + (K_1C-K_2)(T-T_0),$$

in which v and  $V_0$  are the surface tensions in dynes per centimeter of the rolution and solvent, respectively, at absolute Kelvin temperatures T and  $T_0$ , respectively; C is the HN concentration in mole-percent; and  $K_1$  and  $K_2$  are regression coefficients. For HN-hydrazine solutions,  $V_0$ ,  $V_0$ ,  $V_0$ ,  $V_0$ , and  $V_0$  equal 93.82, 213.58, 0.302, and 0.243, respectively, and for HN-water solutions,  $V_0$ ,  $V_0$ ,  $V_0$ ,  $V_0$ , and  $V_0$  equal 92.69, 229.45, 0.220, and 0.248, respectively.

## EXPLOSION CHARACTERISTICS OF HN

## Thermal Stability

The thermal stability of HN at 1 atmosphere pressure in air has been studied by numerous investigators, and there seems to be general agreement that the pure material decomposes explosively at about 300° C. Rosen (25)

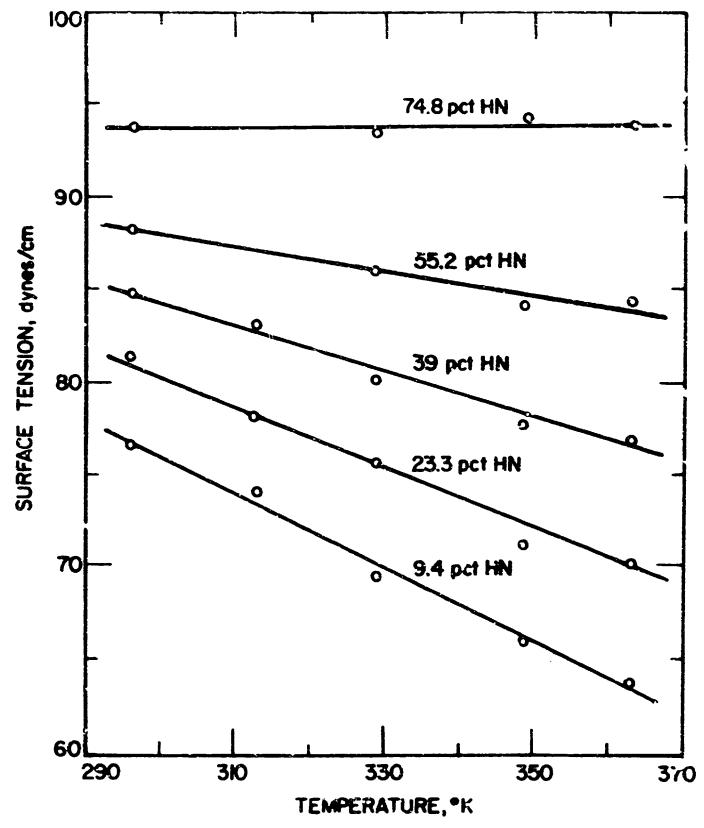


FIGURE 6. - Surface Tension of HN-Hydrazine S. tions at Various HN Concentrations as a Function of Temperature.

measured the ignition temperature of HN using the "Bruceton up-and-down" method (5), which gave a reproducible 50-percent probability of ignition at 307° C.

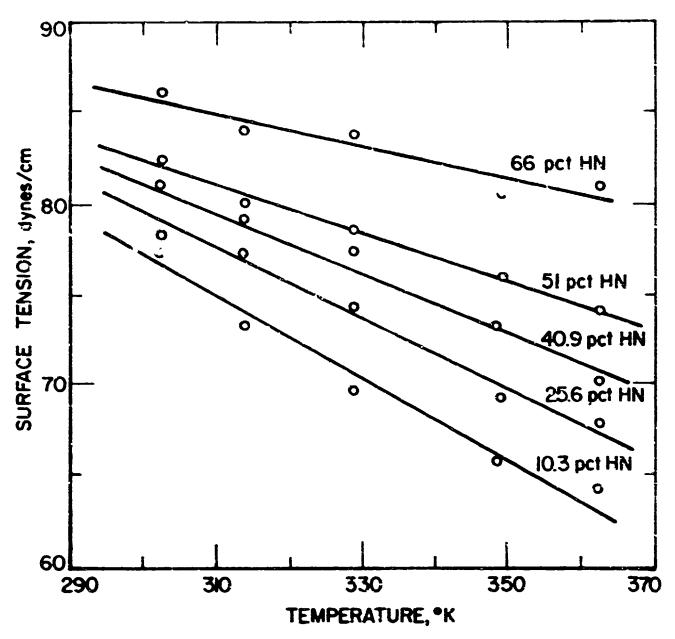


FIGURE 7. - Surface Tension of HN-Water Solutions at Various HN Concentrations as a Function of Temperature.

Additional experiments were conducted by the Bureau with liquid HN to study the initiation of detonations in unconfined films, 0.25 cm thick, by means of electrically heated Nichrome<sup>5</sup> wire and open flames (propane torch). These studies indicate that although unconfined thin films of molten HN support combustion when ignited in air at 1 atmosphere by either method, they do not detonate. Furthermore, the flame was extinguished upon removal of the ignition source. These results agree with those of Shidlovskii and coworkers (27), who could not cause detonation in glass tubes 10, 15, and 20 mm in diameter using electrically heated Nichrone wire. To achieve stable burning, they found that the addition of about 10 weight-percent of potassium dichromate to the hydrazine nitrate was necessary. Levy and coworkers (18) found that a tamped strand of HN (density 0.95 g/cm<sup>2</sup>) containing 2 weight-percent magnesium oxide burned stably in air at 1 atmosphere at a rate of 0.04 cm/sec, but a similar strand of pure HN did not burn.

EReference to specific trade names in this report is made for identification only and does not imply endorsement by the Bureau of Mines.

## Detonation Velocity Measurements

The detonation velocity of molten HN at 75° C was determined by the Bureau in thin-film experiments to be 8,500 m/sec. (See table 2.) Price and coworkers (22) reported a detonation velocity of 8,510 m/sec at a density of 1.59 g/cm³ for a 6.3-cm-diameter charge of pressed HN. Medard (19), using a 30-mm-diameter by 170-cm-long pressed-HN charge, found that the maximum detonation velocity occurred at a density of 1.3 g/cm³. Moreover, Price and coworkers established that such maximums are likely to occur for explosives for which the critical diameters increases with density. The results of these investigations are shown in figure 8. From these results it was concluded that the critical diameter of HN increases with increasing packing density. Price and coworkers found that the infinite charge diameter detonation velocity, V, for HN in meters per second can be expressed as

V = 5,390 pHN - 100,

in which OHN is the density of HN in grams per cubic centimeter. Michel and coworkers (20) computed a Chapman-Jouguet deconation velocity of 5,840 m/sec for a density of 1.0 g/cm<sup>3</sup>; however, the expression found by Price and coworkers gives a value of 5,290 m/sec.

TABLE 2. - Detonation velocities and critical film thicknesses (crt)
of both low-velocity and high-velocity detonations of
molten HN, HN-water, and HN-hydrazine solutions
at 75° C

Liquid		Detonation velocity			
	HN concen-	High		Low	
Composition	tration,	Velocity,	Cft,	Velocity,	Cft,
	wt pct	m/sec	C m	m/sec	cm
HN	100	8,500	0.127	1,400	1≤0.025
HN-water	85	7,600	. 305	2,400	≤.025
	75	( <sub>s</sub> )	( <sub>s</sub> )	2,100	. 330
	65	$(^3)$	(3)	( <sup>3</sup> )	( <sup>3</sup> )
HN-hydrazine	80	8,600	.076	1,800	≤.025
· ·	60	8,200	.076	( <sup>2</sup> )	(°2)
	40	7,800	.254	2,200	.076
1	20	( <sup>3</sup> )	$\binom{3}{3}$	( <sup>3</sup> )	$(^3)$

<sup>19.025</sup> cm represents the limit of resolution of the apparatus.

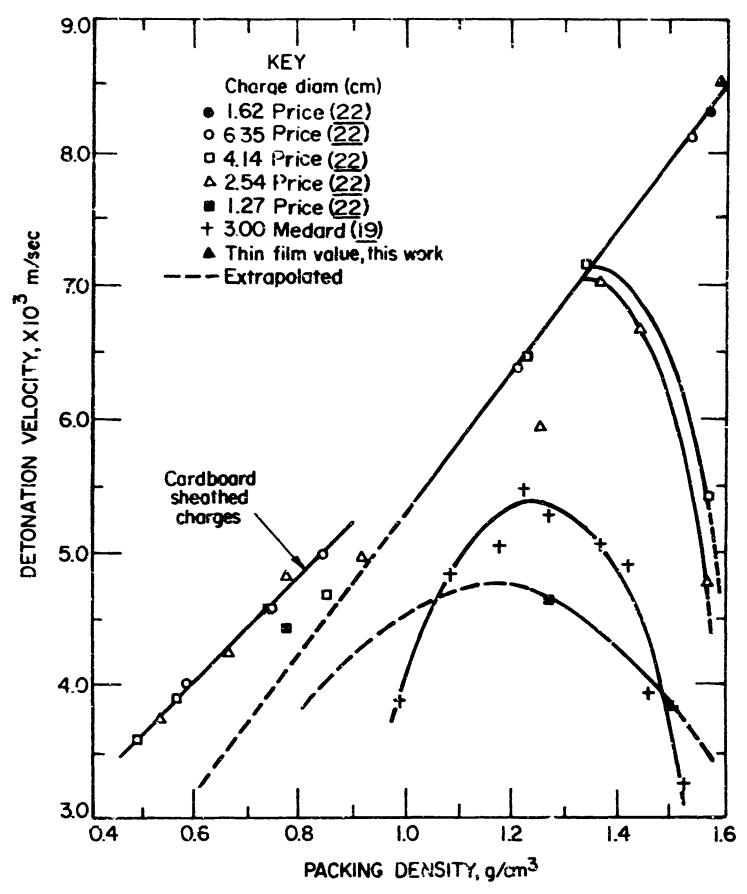
#### TNT Equivalence

Among the methods used for testing the strength of explosives is the ballistic mortar test (30). In this method a known charge of explosive is placed in a swinging mortar, fitted with a projectile, and exploded with a detonation  $c_{\rm ap}$ . The vertical lift of the mortar due to this explosion is

Not observed.

<sup>3</sup> No propagation.

The critical diameter is the minimum charge diameter at which propagation of a stable detenution is possible.



FICURE 8. - Detonation Velocity of Pressed HN as a Function of Density for Various Charge Diameters.

mensured in inches. The vertical lift relative to that of TNT is known as the TNT equivalence of the explosive. The ballistic mortar is capable of quickly feeding those materials that exhibit exothermic reactions with reaction rates greater than about 0.1 second. In Bureau experiments, the TNT equivalence of HN was 142 compared to granular TNT.

## Impact Sensitivity

Impact sensitivity tests, using the "Bruceton up-and-dow method (5), gave values for 50-percent probability for ignition of 175 kg-cm for the cup and plunger and 50 kg-cm for the ERL type 12 tool test (10) procedures. In similar experiments, Smith and Walton (28) reported a value of 32 kg-cm for a 50-percent probability for the ERL type 12 tool. Medard (19) obtained values of 200 to 250 kg-cm.

#### EXPLOSION CHARACTERISTICS OF SYSTEMS CONTAINING HN

#### Detonation Velocity of HN-Hydrazine and HN-Water Solutions

Both the thin-film detonation velocity and the critical film thickness were determined by measuring the velocity of the detonation as it traveled through a wedge of the solution and by observing the film thickness at which the detonation was extinguished. The experimental apparatus (23) consisted of an open, plastic wall tray, with a 1.25-cm steel base, inclined at a slight angle so that the contained liquid formed a wedge, the thickness of which varies from one-quarter inch to zero. The initiating charge consisted of a 20-gram tetryl pellet formed from two pills, each 4.1 cm in diameter and 1.3 cm thick. The initiating charge was separated from the liquid by the 0.08-cm-thick Plexiglas container wall. The results revealed the occurrence of both a high- and a low-velocity detonation. The high-velocity detonation (7,600 to 8,500 m/sec) started near the initiating explosive and converted to a low-velocity detonation (1,400 to 2,400 m/sec) when the film reached the critical thickness for the high-velocity detonation. Table 2 presents a summary of these results.

For comparison, the range of detonable compositions of the ternary system, HN-hydrazine-water, as determined by Dwiggins and Larrick (7), is presented in figure 9. Their apparatus consisted of a 7.5-cm-long brass pipe with a 2.5-cm inside diameter and a 4.1-cm outside diameter and with a 1-mil corper foil soldered over one end. A 50-gram tetryl pellet, 2.5 cm long and 4.1-cm in diameter, was used to initiate the test solution. A steel witness plate, 10 by 10 cm, by 0.95 cm thick, was used to indicate a detonation. In the Rureau's work, the thin-film binary HN solutions which were detonated fell within the "detonable" region of the ternary triangle of figure 9. Similarly, Bureau data also showed that HN solutions which did not detonate were outside the "detonable" region. Dwiggins and Larrick (7) showed that HN-hydrazine solutions containing less than 25 percent by weight HN, HN-water solutions containing less than 55 percent by weight of water were not detonable under their experimental conditions.

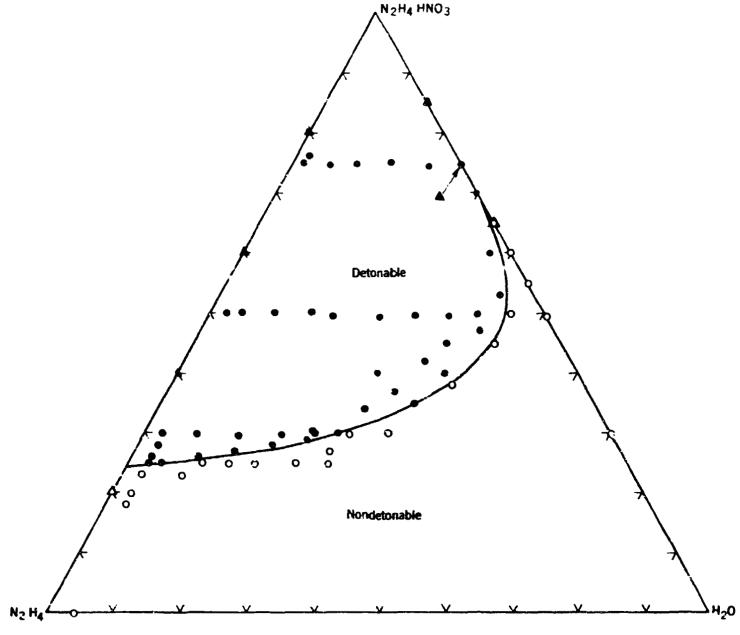


FIGURE 9. - Detonable Compositions of the Ternary System, HN-Hydrazine-Water.

## Compatibility Studies of HN With Various Materials

Compatibility studies of HN with various hypergolic propellants showed that crystalline HN and liquid nitrogen tetroxide react vigorously on contact. Moreover, a differential-scanning-calorimeter study of a frozen mixture containing equal propertions by volume of HN and nitrogen tetroxide initially at -100° C showed that such mixtures react exothermically when the temperature is raised to -40° C. This is a significantly lower temperature that the melting point of nitrogen tetroxide, -11.2° C.

Another experiment was made to determine if the hypergolic reaction that results when HN contacts with nitrogen tetroxide would be capable of initiating a detonation in the HN. In this study, liquid nitrogen tetroxide was forcibly injected under the surface of 200 cm<sup>3</sup> of molten HN contained in glass vessels; similar experiments were performed with detonable HN-hydrazine and

HN-Aerozine-50 solutions. Although considerable reaction was evident, none of the reactions approached an explosion.

Sabanejeff (26) reported that HN reacted with concentrated sulfuric acid with a violent evolution of nitric oxide. At -15° C this reaction no longer took place, but it set in at once if the mixture was removed from the cooling medium. Sulfuric acid 14° decomposed HN upon heating, with evolution of hydrazoic acid. When HN was mixed with phosphorus pentachloride, particularly if the two compounds were rubbed together, deflagration occurred with formation of hydrazine dichloride.

Extensive compatibility studies have been conducted on HN by many investigators. Medard (19) found that weakly nitrated explosives could be appreciably sensitized by a small amount of HN. Hodgkinson (14) reported that detonation occurred 40 percent of the time if cobalt cubes were dropped into molten HN and 20 percent of the time if nickel cubes were used. Similar experiments conducted in this investigation with heated molybdenum chips and molten HN showed no evidence of a violent reaction. Hodgkinson attributes the reaction to the formation of a small amount of metal azide on the metal cubes, which explosively decomposes and detonates the remaining HN.

Lee (17) and Dwiggins and Larrick (7) investigated the relative compatibility of the ternary HN-hydrazine-water system with various construction materials. They found, for example, that polyethylene, polystyrene, Teflon, nylon, titanium, and tantalum showed no evidence of being incompatible with the ternary system.

## SUMMARY

Since the  $\beta$  crystalline form of HN is unstable, this investigation resulted in additional information only on the  $\alpha$  crystalline form of HN. The heat of conversion from the  $\beta$  to the  $\alpha$  form is 2.0 kcal/mole, and no additional phase changes occur in the  $\beta$  form from -70° C to its melting point at about 70° C. As an additional aid for identification, the infrared and X-ray spectra of HN were obtained. HN weight-loss rates were measured at elevated temperatures.

The densities for given concentrations of HN in either hydrazine or water are satisfactorily represented by the equation  $\rho = \rho_0 + aN + bN^2$ . Similarly, the expressions describing the kinematic viscosity as a function of absolute temperature and HN concentration in hydrazine and water are  $\log_{10} \frac{V}{V_0} = K \frac{N}{T}$  and  $\log_{10} \frac{V}{V_0} = K \frac{N^2}{T}$ , respectively. The surface tensions of molten HN and various HN-hydrazine and HN-water solutions at elevated temperatures were measured and found to be satisfactorily represented by the expression,  $Y = Y_0 + (K_1 C - K_2)(T - T_0)$ .

HN was found to decompose explosively at about 300° C. The detonation velocity for a pure HN film was found to be 8,500 m/sec, which agrees with the values obtained by other investigators for cylindrical charges. The ball\_stic

mortar showed a TNT equivalence of 142 for HN. Impact sensitivity tests gave 50-percent probability for ignition at drop-weight heights of 175 kg-cm, 50 kg-cm for cup and plunger, and 10 kg-cm for ERL type 12 tool test procedures.

Thin-film detonation studies have shown that molten HN, or HN-hydrazine and HN-water solutions having HN concentrations of at least 40 and 75 percent, respectively, exhibit stable detonations; HN-hydrazine and HN-water solutions containing 20 and 65 weight percent HN or less, respectively, do not support stable detonations.

HN, HN-hydrazine, and HN-Aerozine-50 solutions were found to be incompatible with nitrogen tetroxide; although considerable reaction was evident, none of the reactions approached an explosive magnitude. Other investigators have reported detonative reactions of HN with, for example, cobalt and nickel. In similar experiments, the Bureau found no violent reaction when heated molybdenum chips were dropped into molten HN.

#### ACKNOWLEDGMENT

The authors are pleased to acknowledge the support of this work by National Aeronautics and Space Administration (NASA) Manned Spacecraft Center, Houston, Tex., under N.SA Order No. T-39882(G). Of considerable help in this investigation were the following personnel of the Bureau's Safety Research Center. Mrs. Jean L. Seiler (physical science technician), who did all the experimental measurements of viscosity, surface tension, and density; John Ribovich (research chemist), who measured the detonation velocities in thin-films; and John Queiser (physicist): who obtained the infrared absorption spectra of HN.

#### REFERENCES?

- 1. Barlot, Jean, and Simone Marsaule. Studies of Binary Systems; Hydrazine Nitrate and Alkaline Salts. Com. t. rend., v. 226, 1948, pp. 1981-1982.
- 2. Bright, Norman F. H., and Thomas Carson. The Determination of the Heat of Aqueous Solution of Some Hypophosphites and Certain Other Materials. Canadian J. Technol., v. 31, 1953, pp. 221-230.
- 3. Clark, C. C. Hydrazine. Mathieson Chemical Corp., Baltimore, Md., 1953, pp. 19-29.
- 4. Corcoran, Jane M., Howard W. Kruse, Sol Skolnik, and Eugene Lieber. Thermal Analysis of the System Hydrazine Nitrate-Water-Hydrazine. U.S. Naval Ord. Test Station, Inyokern, China Lake, Calif., NAVORD Rept. 2087, Jan. 26, 1954, 13 pp.
- 5. Crow, Edwin L., Frances A. Davis, and Margaret W. Maxfield. Statistics Manual. Dover Publications Inc., New York, 1960, p. 93.
- 6. Curtius, Theodor, and Rudolf Jay. Diazo- und Azoverbindungen der Fettreihe. IV. Abhandlung. Ueber das Hydrazin (Diazo and Azo Combinations of the Aliphatic Series. IV. Treatise on Hydrazine). J. prakt. Chem., v. 147, 1889, p. 27.
- 7. Dwiggins, R. D., and B. F. Larrick. Investigation of Mixtures of Lydrazine, Hydrazine Nitrate and Water, Part II. Progress Report covering the period from Apr. 1 to June 30, 1952. U.S. Naval Ord. Lab. Rept. 2563, Aug. 13, 1952, 15 pp.
- 8. Elverum, Gerald W., Jr. and Leland G. Cole. Some Physical-Chemical Studies of the System Hydrazine-Hydrazine Nitrate-Water. Jet Propulsion Lab., Calif. Inst. Technol, Pasadena, Calif., Memo. 20-79, Dec. 30, 1952, 13 pp.
- 9. \_\_\_\_. Some Physical-Chemical Studies of the System Hydrazine-Hydrazine Nitrate and Water. Jet Propulsion Lab., Calif. Inst. Technol., Pasadena, Calif., Mero. 20-152, Dec. 22, 1957, 46 pp.
- 10. Eyster, E. H., and L. C. Smith. Studies of the ERL Type 12 Drop-Weight Impact Machine at NOL. U.S. Naval Ord. Lab. Memo. 10,003, Jan. 25, 1949, 29 pp.
- 11. Eyster, E. H., L. C. Smith, and S. R. Walton. The Senticivity of High Explosives to Fure Shocks. U.S. Naval Ord. Lab. Memo. 10,336, July 14, 1979, 39 pp.

Titles enclosed in parenths s are translations from the language in which the item was originally lished.

- 12. Furman, N. H. (ed.). Scott's Standard Methods of Chemical Analysis.
  D. Van Nostrand, New York, v. 1, 5th ed., 1939, p. 605.
- 13. Glatts, G. 3. Stability Tests of Rinopropel' into exposed to Flames and Rifle Fire. Jet Propulsion Lab., Calif. Inst. Teck: 1., Pasadena, Calif., Tech. Rept. 32-172, ab. 26, 1962, 11 pt
- 14. Hodgkinson, W. R. E. Some Reactions of Hydrozima & te, J. Soc. Chem. Ind., v. 32, 1913, pp. 519 529.
- 15. Kissinger, I. W. The Preparation and Properties of Hydractuse Momenitrate. U.S. Naval Ord. Lab. Memo. 10,359, July 7, 1949, 4 pp.
- 16. Lange, Norbert Adolph (ed.). Handbook of Chemistry. Handbook Publishers Inc., Sandusky, Ohio, 5th ed., 1. 4, p. 1594.
- 17. Lee, Donald H. A Survey of the Compatibility of Varines Materials With Hydrazine and Mixtures of Hydrazine, Eydrazine Nitrate, and Water. Jet Propulsion Lab., Calif. Inst. Technol., Pasadena, Calif. emo. 20-152, Dec. 22, 1957, 46 pp.
- 18. Levy, J. B., G. von Elbe, R. Friedman, T. Wallin, and J. J. Adams. The Deflagration of Hydra me Perchlorate. Advanced Propellant Chemistry, ed. by Robert F. Goul American Chemical Society, New York, 1966, p. 63
- 19. Medard, Loris. Propriétés Explos ves du F trate d'Eydrazine (Explosive Properties of Hydrazine Nitrate). Memb. Poudres. v. 34, 1952, pp. 147-157.
- 20. Michel, R. E., G. G. Harms, J. M. Kolpke, R. W. Mueller, W. O. Jacobson, J. R. Syolund, and N. O. Christians. Detonation Reaction Control (Small Impulse Engine). U.S. Air Force Flight Dynamics Lab., Honeywell Inc., Wright-Patterson Air Force Base, Tech. Pos. Rept. FDL-TDP-64-63, March 1964, 90 pp.
- Partington, J. R. An Advanced Treatise of Physical Chemistry: V. 2.
   The Properties of Liquids. Longmans, Green and Co., New York, 1951, p. 185.
- 22. Price, Donna, T. P. Liddiard, Jr., and R. D. Drosd. The Detonation Behavior of Hydrazine Mononitrate. U.S. Naval 'rd. Lab., Rept. NOLTR-66-21, Apr. 15, 1966, 15 pp.
- 23. Ribovich, J. A Wedge Technique for Evaluation of Decomation Hazards of Liquid Explosives. Ann. New York Acad. Sci., v. 152, Art. 1, Cat. 28, 1968, pp. 7-5-772.
- 24. Robinson, Robert J., and Walter C. McCrone. Hydrazias Nitrate (1). Anal. Chem., v. 30, 1958, pp. 1014-1015.

- 25. Rosen, J. M. A New Apparatus for the Determination of the Ignition Temperature of Explosives. U.S. Naval Ord. Lab. Memo. 10,289, Dec. 21, 1949, 21 pp.
- 26. Sabanejeff, A. Ther einige anorganische Hydrazinsalze und über die Darstellung der Stickstoffwasserstoffsäure (Some Inorganic Hydrazine Salts and the Preparation of Hydrazoic Acid). Ztschr. anorg. Chem., v. 20, No. 1, March 1899. pp. 21-29.
- 27. Shidlovskii, A. A., V. I. Simishin, and V. I. Simitin. (Thermal Decomposition of Combustion of Hydrazine Nitrate.) J. Appl. Chem. (U.S.S.R.), v. 33, No. 6, 1960, pp. 1411-1413.
- 28. Smith, L. C., and S. R. Walton. Miscellaneous Physical Testing of Explosives. U.S. Naval Ord. Lab. Memc. 10,381, Sept. 21, 1949, 9 pp.
- 29. Sommer, Fritz. Studien über das Hydrazin und seine anorganischen Derivate (Studies on Hydrazine and its Inorganic Derivatives. II. Monotropism of Hydrazine Nitrate). Ztschr. amorg. Chemie, v. 86, No. 1, Feb. 27, 1314, pp. 71-86.
- 30. Taylor, J., and J. H. Cook. Improved Operation of the Ballistic Mortar for Determining the Power of High Explosives. J. Sci. Instr. and Phys. in Ind., v. 26, No. 8, 1949, pp. 266-268.
- 31. Vango, Stephen P., and John B. Krasinsky. Density, Vapor Pressure, and Viscosity of Solutions of Hydrazine Mononitrate in Hydrazine. Jet Propulsion Lab., Calif. nst. Technol., Pasadena, Calif., Tech. Memo. 33-103, Oct. 15, 1962, 12 pp.

#### APPENDIX. -- SUMMARY OF PROPERTIES OF HA

This appendix presents the work of other investigators on HN and multicomponent systems containing HN that was not cited with the Bureau work because of its indirect relationship.

Table A-1 summarizes the physical properties of HN obtained by various investigators. Similarly, table A-2 lists the combustion characteristics of HN and of an HN-hydrazine solution obtained by other researchers.

Figures A-1, A-2, A-3, and A-4 present the data of investigators regarding physical properties of systems containing HN. Figure A-1 shows the heat of solution of HN  $(8)^1$  in water-hydrazine systems for different compositions of the three components. Figure A-2 gives the vapor pressure for two HN-hydrazine solutions (31). Figure A-3 shows the liquidus isotherms for the ternary system HN hydrazine-water (4), and figure A-4 gives the liquidus line for the binary system HN-ammonium nitrate (1).

Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

TABLE A-1. - Physical properties of NN and multicomponent systems containing and

Property	Description or value	Reference
Crystal morphology data:		
Crystal system	Monoclinic	Robinson (24).
Form and habit	Tablets and rods	Do.
Axial ratio	a:b:c=0.957:1:0.492	Do.
Interfacial angle (polar).	88°26'	Do.
Crystal angle	90°	Do.
X-ray diffraction data:		
Cell dimensions	11.23A by 11.73A by 5.17A	Do.
Formula weights per cell	8	Do.
Formula weight	95.06	Do.
Density	1.661 g/cm <sup>3</sup>	Do.
Optical properties: Refractive indices (5,893A; 25° C):		
β	1.458 ± 0.003	Do.
a	1.605 ± 0.004	Do.
G. C.	1.620 ± 0.005	Do.
Optic axial angles (5,893A; 25°C): 2V  ZE Dispersion Sign of double refraction.	33° 54° r>V Negative	Do. Do. Do. Do.
Molecular refraction (R) (5,893A; 25°C):		
³√a.b	1.559	90.
R (calcd)	19.6	Do.
R (obsd)	18.4	Do.
Melting points:		
ß form	62.5° C	Do.
	62.09° C	Sommer (29).
a form	70.5° C	Robinson (24).
	70.70° C	Sommer (29).
Heat of formation	59.8 kcal/mole	Shidlovskii (27).
	50.9 ical/mole	Elverum (9).
Heat of solution:		
Water	-8.72 kcal/mole	Bright $(2)$ .
Extrapolated value	-9.3 kcal/mole	Elverum (9).
Hydrazine (extrapolated		
value)	+3.7 kcal/mole	Do

TABLE A-2. - Explosion characteristics of HN and multicomponent systems containing HN

Characteristic	Description or value	Comment	Reference
Ignition temperature		Obtained from bonfire tests.	Glatts ( <u>13</u> ).
Decomposition process	4N <sub>€</sub> H <sub>5</sub> NO <sub>5</sub> →5N <sub>2</sub> - 2NO + 10H <sub>2</sub> O	Gas analysis in an evacuated vessel at 200° C.	Hodgkinson (14).
Carc gap sensitivity	6.25 cm	Card attenuators of Aerowax B cast to desired thickness.	Eyster ( <u>11</u> ).
Brisance	82	Cast TNT≈100	Ribovich (25).
Flame temperature	2,400° C	•	Medard (19).
Ternary solution sensitivity to projectile impact.	Detonated when impacted by high-explosive incendary projectile.	high-explosive	Glatts ( <u>13</u> ).

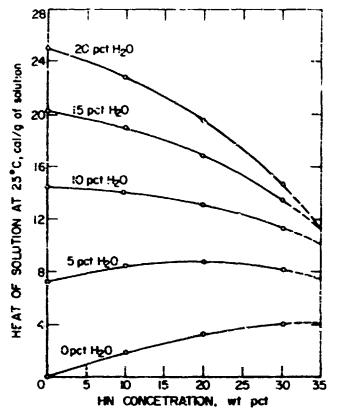


FIGURE A-1. - Heats of Solution of HN and Water in Hydrazine.
From Elverum (§).

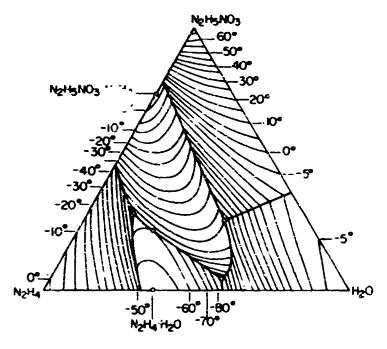


FIGURE A-3. - Vapor Pressure for Water, Hydrazine, and Two HN-Hydrazine Solutions.

From Vango (31).

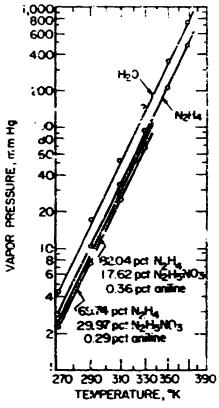


FIGURE A-2. - Three Component Liquidus Isotherms for the Ternary Sysiem HN-Hydrazine-Water-From Corcoron (4).

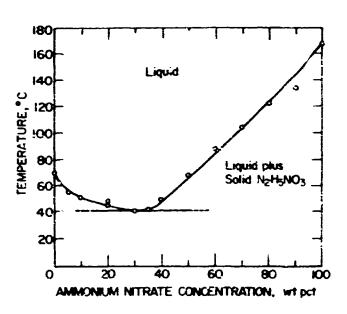


FIGURE A-4. - Liquidus Line for the Binary System HN-Ammonium Nitrate. From Barlot (1).